



NO_x storage and reduction over copper-based catalysts. Part 2: Ce_{0.8}M_{0.2}O₈ supports (M = Zr, La, Ce, Pr or Nd)

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ARTICLE INFO

Article history:

Received 11 April 2016

Received in revised form 24 May 2016

Accepted 27 May 2016

Available online 28 May 2016

Keywords:

NSR
deNO_x
Diesel aftertreatment
Copper catalyst
Ceria
DRIFTS
Operando

ABSTRACT

5% copper catalysts with Ce_{0.8}M_{0.2}O₈ supports (M = Zr, La, Ce, Pr or Nd) have been studied by rapid-scan *operando* DRIFTS for NO_x Storage and Reduction (NSR) with high frequency (30 s) CO, H₂ and 50%CO + 50%H₂ micropulses. In the absence of reductant pulses, below 200–250 °C NO_x was stored on the catalysts as nitrite and nitro groups, and above this temperature nitrates were the main species identified. The thermal stability of the NO_x species stored on the catalysts depended on the acid/basic character of the dopant (M more acidic = NO_x stored less stable \Rightarrow Zr⁴⁺ < none < Nd³⁺ < Pr³⁺ < La³⁺ \Leftarrow M more basic = NO_x stored more stable). Catalysts regeneration was more efficient with H₂ than with CO, and the CO + H₂ mixture presented an intermediate behavior, but with smaller differences among the series of catalyst than observed using CO alone. N₂ is the main NO_x reduction product upon H₂ regeneration. The highest NO_x removal in NSR experiments performed at 400 °C with CO + H₂ pulses was achieved with the catalyst with the most basic dopant (CuO/Ce_{0.8}La_{0.2}O₈) while the poorest performing catalyst was that with the most acidic dopant (CuO/Ce_{0.8}Zr_{0.2}O₈). The poor performance of CuO/Ce_{0.8}Zr_{0.2}O₈ in NSR experiments with CO pulses was attributed to its lower oxidation capacity compared to the other catalysts.

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1. Introduction

Ceria-based oxides have been used in catalysts for gas pollution control in gasoline vehicles since the beginning of the 1980s [1–4], when they were incorporated into Three Way Catalysts for simultaneous NO_x, CO and hydrocarbons abatement. Even at this early stage, researchers realized that the catalytic performance of cerium oxide was improved by doping with other cations such as Zr⁴⁺, and Ce–Zr mixed oxides showed higher thermal stability, better reducibility, higher oxygen storage capacity and enhanced oxidation activity compared to cerium oxide alone.

It has been also reported that ceria doping with foreign cations has benefits in other catalytic applications related to gas pollution control in vehicles. Ceria is an excellent catalyst to accelerate soot combustion and regenerate Diesel Particulate Filters (DPF) [5–9]. However, pure ceria sinters readily and losses activity drastically under the highly demanding thermal and chemical operational conditions on these DPFs, and ceria doping with other cations such as those of Zr, Pr or La, among others, is essential in order to achieve

suitable thermal stability. Dopants also enhance the production of active oxygen, which is responsible for the high soot oxidation capacity of the ceria-based oxides.

Cerium oxides have been also studied for NO_x removal in Diesel exhausts using the NSR technology [9–11], where NO_x is stored on the catalyst and a reductant is fed periodically into the exhaust gas stream to reduce the stored NO_x species. It has been reported that the NSR performance of Pt/Ceria is improved upon doping ceria with Pr, because Pr accelerates the oxidation of adsorbed NO_x species and destabilizes these species when the reductant is fed [12]. It has been also reported [13] that the thermal stability of Pt/Ceria NSR catalysts is improved by La, Pr and/or Zr doping, and that these materials were active even after hydrothermal aging at 700 °C.

However, to the best of our knowledge, the utilization of copper-based noble metal-free formulations containing solid solutions of ceria with other dopants as NSR catalysts has not been reported, and the goal of the current article is to study this type of materials.

In a previous article [14], copper catalysts were studied by *operando* DRIFTS-MS-Chemiluminescence in the NSR process using H₂ and CO as reductants, and CeO₂, BaO and BaO + CeO₂ supports were compared. CeO₂ and BaO did not form solid solutions in any appreciable extent, and mixtures of oxides/carbonates were obtained. It was concluded [14] that the copper catalysts with

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cerium and/or barium oxide/carbonate supports were able to chemisorb NOx at 400 °C, and at this temperature, the general NSR behavior of all catalysts was quite similar. Differences were only observed when using high frequency (30 s) pulses of CO, where CuO/CeO₂ showed the best recovery of NOx storage capacity, and NOx chemisorption and desorption rates were faster for CuO/CeO₂ than for CuO/BaO.

The goal of the current article is to report performance of NSR copper catalysts with ceria supports doped with different metal cations, with an aim to improve the NSR performance of CuO/CeO₂. Copper catalysts with Ce_{0.8}M_{0.2}O₈ supports (M = Zr, La, Ce, Pr or Nd) have been studied by *operando* DRIFTS-MS-Chemiluminescence. Realistic periods of lean operation (30 s) similar to those originally proposed by Toyota in the mid 1990s [15] and periodic micropulses of reductant were used. Rapid-scan DRIFTS was performed in a spectrometer that is able to obtain up to 17 spectra per second.

2. Experimental details

2.1. Catalysts preparation

Ce_{0.8}M_{0.2}O₈ supports (M = Zr, La, Ce, Pr or Nd) were prepared with the following precursors: ZrO(NO₃)₂·xH₂O (~27% Zr), La(NO₃)₃·6H₂O (≥99.0%), Ce(NO₃)₃·6H₂O (99.5%), Pr(NO₃)₃·6H₂O (99.9%) and Nd(NO₃)₃·6H₂O (≥99.9%).

Aqueous dissolutions of the required precursors were prepared with 10 ml of solvent, using the required amounts to obtain 5 g of each mixed oxide. The solutions were introduced into a muffle furnace previously heated at 200 °C, and after 1 h, the temperature increased at 10 °C/min until 500 °C, holding the samples at this temperature for 2 h. As previously reported, the Ce_{0.8}M_{0.2}O₈ supports with M = Zr, La, Pr or Nd dopants [16] form mixed oxides where M is located within the parent ceria lattice.

CuO/Ce_{0.8}M_{0.2}O₈ catalysts were prepared with a 5 wt.% target Cu loading. The required amount of Cu(NO₃)₂·5·(1/2)H₂O (98%) was dissolved in 2 ml of water and 2.5 g of each support was impregnated with this solution. The impregnated supports were heat treated following the same protocol used for the supports preparation, that is, they were introduced in a muffle furnace previously heated at 200 °C, and after 1 h, the temperature was increased at 10 °C/min until 500 °C, holding this temperature for 2 h. Details regarding catalyst characterization are reported elsewhere [16], but BET surface area values are included here, and were 60, 40, 58, 35, and 45 m²/g for catalysts with M = Zr, La, Ce, Pr and Nd, respectively.

2.2. NOx chemisorption and NSR experiments

NOx chemisorption and NSR performance were studied in a Shimadzu (IR Tracer-100) Fourier Transform Infrared Spectrometer with a Harrick reaction cell coupled to an EcoSys-P mass spectrometer and a chemiluminescence NOx analyzer (Thermo 42H). The sample holder of the DRIFT cell was 6.3 mm diameter with a height of 3.3 mm which was filled with sample (100 mg in the absence of diluent). It is important to note that the infrared spectrum only provides information on the top <0.2 mm of this sample [17].

The reaction cell was designed to allow the reaction gas mixture (50 ml/min; 850 ppm NOx + 5% O₂ + N₂) to pass through the catalyst bed with the gas exit under the bed.

It is worth mentioning that temperature control and determination in DRIFTS cells is problematic. It has been reported that the actual temperature of the catalyst bed can be significantly lower than the set temperature, with differences of around 50 °C when operating at 400 °C [18]. This must be kept in mind when cross referring to data obtained using other devices including reactors.

Three types of experiments were carried out: Temperature programmed NOx storage experiments, isothermal NOx storage at 400 °C and Isothermal NOx Storage and Reduction (NSR) at 400 °C.

In temperature programmed NOx storage experiments, the temperature was increased until 150 °C in N₂ flow, and was held at this temperature for 15 min. A background spectrum of the catalyst was recorded at 150 °C in N₂, and then, the inert gas was replaced by NOx/O₂/N₂ and the temperature increased at 10 °C/min until 500 °C. DRIFT spectra and chemiluminescence NOx measurements were simultaneously recorded. 33 scans were averaged to obtain each spectrum, which were measured in the range 4000–1000 cm⁻¹ at 4 cm⁻¹ resolution.

For isothermal NOx storage experiments at 400 °C, the temperature was increased from room temperature to 400 °C under N₂. A background spectrum of the catalyst was recorded at 400 °C, and then the inert gas was replaced by the NOx/O₂/N₂ mixture, considering this as time = 0 min. DRIFT spectra and chemiluminescence NOx measurements were simultaneously recorded with time until saturation of the catalysts. In these experiments, the settings used to obtain the spectra were the same as in previous temperature programmed NOx storage experiments.

Isothermal NOx storage and reduction (NSR) experiments were carried out following the protocol described for isothermal NOx storage experiments at 400 °C, but 100 µl pulses of 100% CO, 100% H₂ or 50% CO + 50% H₂ were additionally fed with frequencies of 30 s. This frequency is in the range of realistic values for application of the NSR technology, as developed by Toyota [15,19,20]. In these experiments, the DRIFT spectrometer was operated in the rapid-scan mode, and one DRIFT spectrum was recorded per second as an average of 7 scans, which were recorded with a resolution of 8 cm⁻¹ in the 4000–1000 cm⁻¹ range. The Rapid-scan Software (Shimadzu Corporation) was used to handle the large volume of data generated. The gas composition was monitored in these experiments with the mass spectrometer. This detection technique was used instead of chemiluminescence due to the higher sampling frequency of the mass spectrometer, which was more convenient for fast screening during pulse experiments. Previous comparison of the NOx concentrations measured by chemiluminescence and mass spectrometry (*m/z* 30) confirmed that both techniques provide comparable results. The benefit of chemiluminescence is that is able to distinguish between NO and NO₂ while the *m/z* 30 signal shows the NOx sum (*i.e.* = NO + NO₂).

3. Results and discussion

3.1. Temperature programmed NOx storage experiments

Fig. 1 shows the NOx (Fig. 1a) and NO₂ (Fig. 1b) profiles monitored during temperature programmed experiments with the chemiluminescence NOx analyzer. All catalysts chemisorbed NOx and oxidized NO to NO₂ in the range of temperatures screened. NOx storage on a NSR catalyst usually depends on its NO oxidation capacity, because NO₂ is more readily chemisorbed than NO, and on the capacity of the NOx storage component. The NO₂ profiles (Fig. 1b) obtained with all catalysts are quite similar, and therefore, differences in NOx profiles (Fig. 1a) must be mainly attributed to the chemisorption capacity of the Ce_{0.8}M_{0.2}O₈ supports.

The dopant loaded to the ceria support affects both the chemisorption of NOx on the catalysts and the stability of the chemisorbed species. Additionally the acid/basic character of the dopants seems to play a major role while the BET surface area of the catalysts seems to be of less relevance. Among catalysts compared, the lowest NOx chemisorption capacity was obtained with CuO/Ce_{0.8}Zr_{0.2}O₈. This catalyst chemisorbed NOx from 150 to 260 °C (Fig. 1a), and the stored NOx species decomposed above

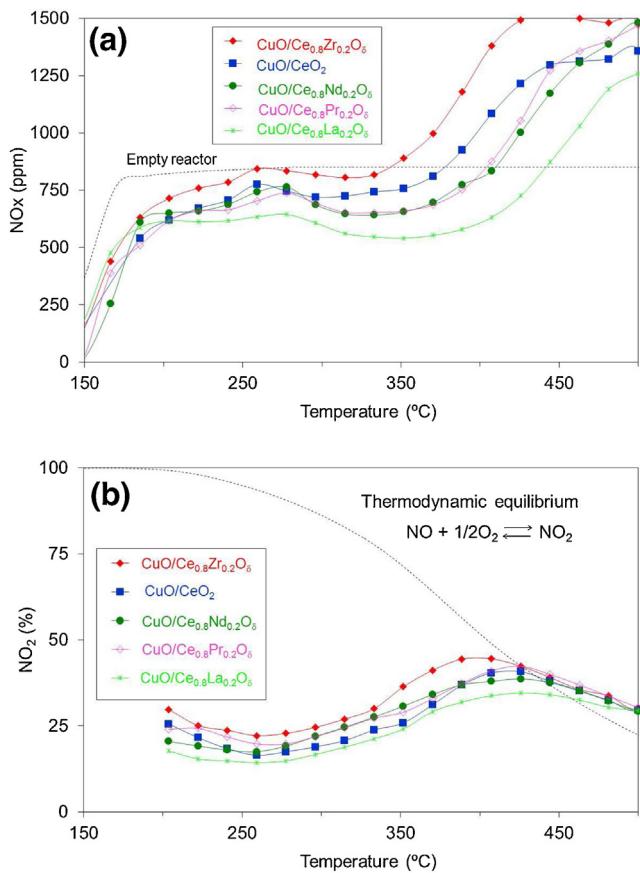


Fig. 1. NO_x concentration (a) and NO₂ percentage with regard to total NO + NO₂ (b) monitored with the chemiluminescence NO_x analyzer during the Temperature Programmed NO_x Storage experiments.

340 °C. The NO_x chemisorption capacity of the dopant-free catalyst (CuO/CeO₂) was higher than that of CuO/Ce_{0.8}Zr_{0.2}O₈, and the decomposition of the nitrogen species stored on CuO/CeO₂ took place above 375 °C. The decrease in the NO_x chemisorption capacity of CuO/CeO₂ upon Zr⁴⁺ doping is consistent with the acidic character of this dopant cation with regard to Ce⁴⁺ (same charge but smaller size), and this acidic character of Zr⁴⁺ is expected to hinder the interaction of the catalyst with NO and NO₂, as these are also acidic gases. On the other hand, La³⁺, Pr³⁺ and Nd³⁺ are more basic than Ce⁴⁺, and all of these improved NO_x storage capacity with regard to CuO/CeO₂ and delayed the release of the stored species to higher temperatures. It is known that the basicity of +3 lanthanide cations (La³⁺, Pr³⁺ and Nd³⁺) decreases with the atomic number (more basic La³⁺ > Pr³⁺ > Nd³⁺ less basic). The ionic radii are quite similar for all of these, and due to the internal location of the 4f electrons, the attraction of the valence electrons by the nuclei increases with the number of protons. This trend in basicity correlates with the behavior of the catalysts, and, for instance, the onset temperature for decomposition of the NO_x species stored on the catalysts (in brackets in °C and in Table 1) followed the same trend as the acid/basic character of the doping cations:

More acidic Zr⁴⁺(340) < none (375) < Nd³⁺ (407) < Pr³⁺ (407) < La³⁺ (444) More basic

The DRIFT spectra recorded during the temperature programmed NO_x storage experiments are compiled in Fig. 2. The most relevant bands of nitrogen- and carbon-containing species appear in this 1700–1200 cm⁻¹ range. All catalysts showed bands related to the formation of nitro, nitrites and nitrates, and the accumulation of these nitrogen species on the catalysts leads to the decomposition of carbonates present on the fresh samples. This was supported

Table 1

Onset temperature for NO_x decomposition in temperature programmed experiments and amount of NO_x stored on the catalysts at 400 °C.

	Onset decomposition temperature (°C)	NO _x stored at 400 °C (μmolNO _x /g _{catalyst})
CuO/Ce _{0.8} Zr _{0.2} O ₈	340	166
CuO/CeO ₂	375	168
CuO/Ce _{0.8} Nd _{0.2} O ₈	407	198
CuO/Ce _{0.8} Pr _{0.2} O ₈	407	368
CuO/Ce _{0.8} La _{0.2} O ₈	444	366

by the decrease in intensity of bands around 1480 and 1350 cm⁻¹ due to carbonate species [21] as a function of temperature.

Before discussing in detail the behavior of the different bands due to nitrogen species observed in Fig. 2, it is worth mentioning that it has been recently reported that the molar absorption coefficients of the overlapping bands of carbonates and nitrates differ. For this reason, the true position of the nitrate and nitrite bands cannot be assessed in such complex spectra [22,23]. However, despite this limitation, some general conclusions can be reached bearing in mind that the exact band positions indicated in the discussion may differ to an extent from those described for other carbonate-free systems.

The first nitrogen species detected on the catalysts at low temperature (150 °C) in Fig. 2 are bridging nitrites ((M–O)₂ = N; band at 1200–1180 cm⁻¹) and nitro groups in some cases ((M–NO₂); band at 1435 cm⁻¹) [24]. There are different mechanisms of nitrite formation upon NO_x chemisorption on ceria, and the most reasonable under the experimental conditions would be the chemisorption of NO on ceria oxygen, where N(II)(NO) is oxidized to N(III)(NO₂⁻). An alternative pathway could be the chemisorption of NO on hydroxyl groups, leading to H₂O release, but this option is ruled out due to the absence of DRIFTS evidence for hydroxyl depletion (bands around 3500 cm⁻¹). An additional option to yield nitrites would be the chemisorption of NO₂ (with N⁴⁺) on reduced Ce³⁺ sites (to yield N³⁺). This pathway could occur under experimental conditions here but with a minor contribution, because NO₂ concentration at 150 °C is much lower than that of NO (Fig. 1b) and Ce⁴⁺ is expected to be much more abundant than Ce³⁺ (the catalysts were calcined at 500 °C and the gas mixture is highly oxidizing). The formation of nitro groups (M–NO₂) could result from NO chemisorption on surface oxygen or the consequence of NO₂ chemisorption on cationic sites.

The increase in temperature leads to the depletion of nitrite bands and to the formation of nitrates, with bands around 1545, 1235 and 1010 cm⁻¹ that could be attributed to monodentate (M–O–NO₂) or bidentate nitrates (M–O₂NO) [24]. The presence of dopants affected the onset temperature for nitrate formation. For instance, nitrate bands were observed at 200 °C on CuO/CeO₂ and CuO/Ce_{0.8}Zr_{0.2}O₈ while 250 °C was required for catalysts with La, Pr or Nd. This would suggest that the low temperature oxidation capacity of CuO/CeO₂ and CuO/Ce_{0.8}Zr_{0.2}O₈ is higher than that of the remaining catalysts under the experimental conditions employed here (note that, as it will be discussed below, the opposite has been observed at 400 °C during reductant pulses).

Additional nitrate bands were identified for some catalysts, which means that nitrate configuration could change with temperature. For instance, the shoulder/band at 1600 cm⁻¹ observed on CuO/Ce_{0.8}Zr_{0.2}O₈ at 300 °C and higher temperatures is consistent with the formation of bridging nitrates ((M–O)₂ = NO).

As a summary, temperature programmed experiments showed that the NO_x storage capacity and the stability of the NO_x species accumulated on the catalysts increases with the basic character of the dopants loaded to ceria, Zr being the most acidic and La the most basic among those studied. The nature of the nitrogen species accumulated on the catalysts depends on temperature, nitrites and

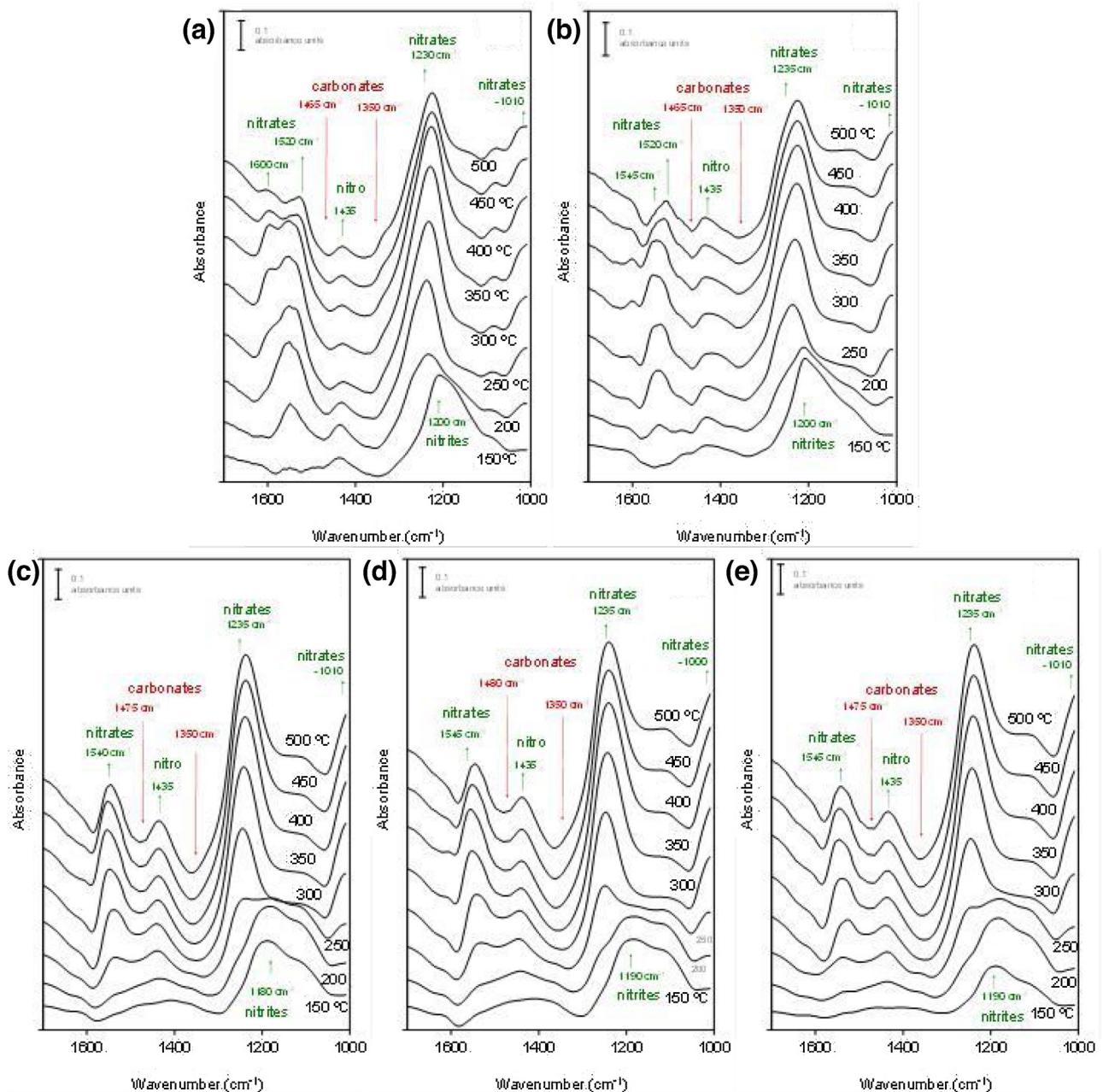


Fig. 2. DRIFT spectra monitored during the Temperature Programmed NO_x Storage experiments with (a) CuO/Ce_{0.8}Zr_{0.2}O₈, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O₈, (d) CuO/Ce_{0.8}Pr_{0.2}O₈, (e) CuO/Ce_{0.8}La_{0.2}O₈.

nitro groups being formed at low temperature (below 200–250 °C) and nitrates at higher temperatures.

3.2. Isothermal NO_x storage at 400 °C

Isothermal NO_x storage experiments were carried out at 400 °C, based on the results of the temperature programmed experiments. As previously mentioned, NO_x chemisorption on a NSR catalyst depends both on the NO oxidation capacity and on the NO_x storage capacity of the support. 400 °C is the temperature for maximum NO₂ production for all catalysts (Fig. 1b), and therefore, the effect of the NO oxidation capacity on NO_x chemisorption can be ruled out, that is, differences in NO_x chemisorption at 400 °C can be only attributed to the NO_x storage capacity.

Fig. 3 shows the NO_x removal profiles at 400 °C. All catalysts chemisorbed NO_x at this temperature, and the NO_x storage capacity was influenced by the selection of the ceria dopant. For instance, CuO/CeO₂ and CuO/Ce_{0.8}Zr_{0.2}O₈ were saturated after 45 min while CuO/Ce_{0.8}La_{0.2}O₈ and CuO/Ce_{0.8}Pr_{0.2}O₈ after 120 min. All basic dopants (La, Pr and Nd) increased the NO_x storage capacity of CuO/CeO₂, and this can be attributed to the stronger interaction of the ceria support with the chemisorbed acidic gases. On the other hand, Zr did not improve the NO_x storage capacity of CuO/CeO₂, and this is also consistent with the acidic character of the Zr⁴⁺ cations.

The amounts of NO_x stored on the catalysts were calculated and are compiled in **Table 1**. The amounts stored on the most efficient catalysts (366 μmolNO_x/g_{catalyst} for CuO/Ce_{0.8}La_{0.2}O₈ and 368 μmolNO_x/g_{catalyst} for CuO/Ce_{0.8}Pr_{0.2}O₈) are similar to the value reported in the literature for a 1%Pt–20%Ba/Al₂O₃ reference cata-

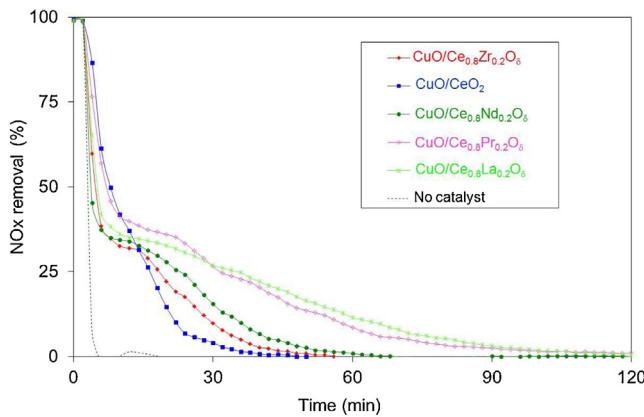


Fig. 3. NOx removal monitored with the chemiluminiscence NOx analyzer in isothermal experiments at 400 °C.

lyst (324 $\mu\text{molNOx/g}_{\text{catalyst}}$ at 400 °C; [25]) and half to that reported for a 1%Pt–10%Ba/Al₂O₃ reference catalyst (714 $\mu\text{molNOx/g}_{\text{catalyst}}$ at 400 °C; [26]). These NOx storage values (in brackets) provide further evidence about the important role of the basicity of the support dopants:

More acidic Zr⁴⁺(166) < none (168) < Nd³⁺ (198) < Pr³⁺ (368) < La³⁺ (366) More basic

The nature of the species formed on the catalysts upon NOx chemisorption at 400 °C was monitored by DRIFTS, and the time-resolved spectra obtained for CuO/Ce_{0.8}Zr_{0.2}O₈ and CuO/Ce_{0.8}La₂O₃ as examples are shown in Fig. 4. All catalysts showed there bands around 1540, 1220 and 1010 cm⁻¹ that can be assigned to monodentate and/or bidentate nitrates, and a small band at 1420 cm⁻¹, which is consistent with the formation of nitro groups [24]. These results confirm the catalytic oxidation of nitrogen from N(II) on NO, which is the main NOx in the fed, mainly to N(V) on nitrates at 400 °C.

Minor differences were found in the time-resolved spectra at 400 °C among catalysts, and only shoulders were detected in some peaks. The most relevant were those observed at 1600 cm⁻¹ on CuO/Ce_{0.8}Zr_{0.2}O₈ which can be assigned to bridging nitrate [24].

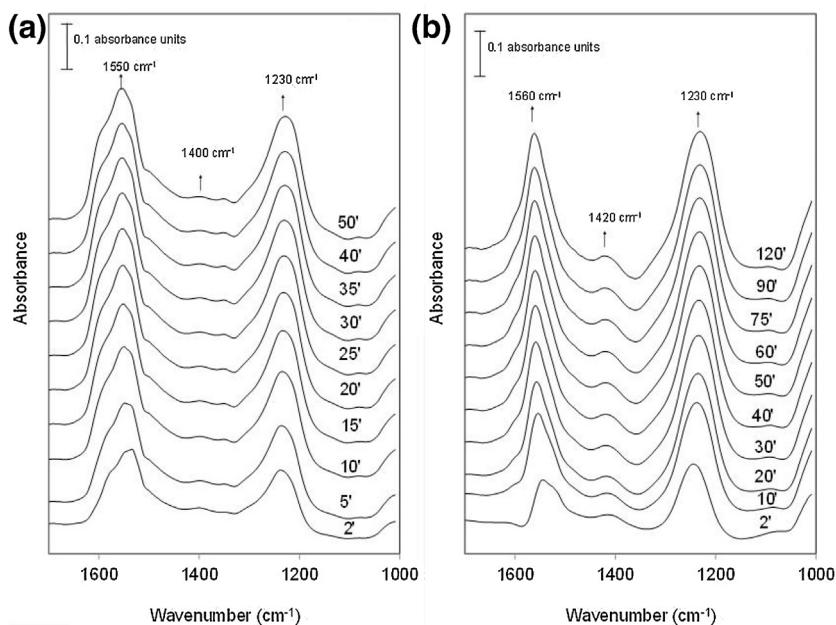


Fig. 4. DRIFT spectra monitored during isothermal experiments at 400 °C with (a) CuO/Ce_{0.8}Zr_{0.2}O₈ and (b) CuO/Ce_{0.8}La₂O₃.

Despite all catalysts form the same species upon NOx chemisorption at 400 °C, this information is relevant for further comparison with the performance in the NSR tests discussed in the next section, where differences were noticed in the chemisorbed nitrogen species while reductants pulsing.

3.3. Isothermal NOx storage and reduction (NSR) at 400 °C

NOx storage and reduction experiments were performed at 400 °C using pulses of CO, H₂ or 50% CO + 50% H₂ at 30 s frequency. The NOx concentrations monitored during the experiments following the *m/z* = 30 signal are included in Fig. 5 for all catalysts.

Over short periods, peaks appear in the *m/z* 30 profile because of NOx slip, that is, once the reductant pulse was fed, part of the NOx stored on the catalyst was reduced but a fraction was released without undergoing reduction.

Over longer time periods, the trend in the *m/z* 30 signals depended on which reductant was pulsed and on the nature of the catalyst. For all catalysts, full regeneration was not achieved with pure CO, and the *m/z* 30 signals increased with time. On the other hand, the *m/z* 30 decreased when H₂ was fed, indicating that the catalysts were being regenerated and that part of the NOx previously stored during CO pulses were removed by H₂. The better performance of H₂ compared to CO was also previously reported for Pt/Ba/Al₂O₃ NSR catalysts [26–28]. Behavior and effectiveness of the mixed CO + H₂ pulses was in between that of CO and H₂, and the catalysts reached stable levels of NOx removed.

The longer-term trend of the NOx concentrations was analyzed in greater detail, by employing a fitting of the *m/z* 30 signals as shown in the example included in Fig. 5c for H₂ pulses. The NOx concentration at the beginning of each pulse was taken for the fitting, and trend lines were obtained. These trend lines are included in Fig. 6 after normalization by dividing all data corresponding to each trend line by the NOx concentration of the first point of each series, that is, all trend lines start with a value of 1, and relative changes were plotted. Also, the time scales used in Fig. 6 were set by considering time = 0 min at the beginning of the first pulse of each series.

Pure CO was ineffective at regenerating the catalysts (Fig. 6a), and all trend lines increased with time. Nevertheless, differences

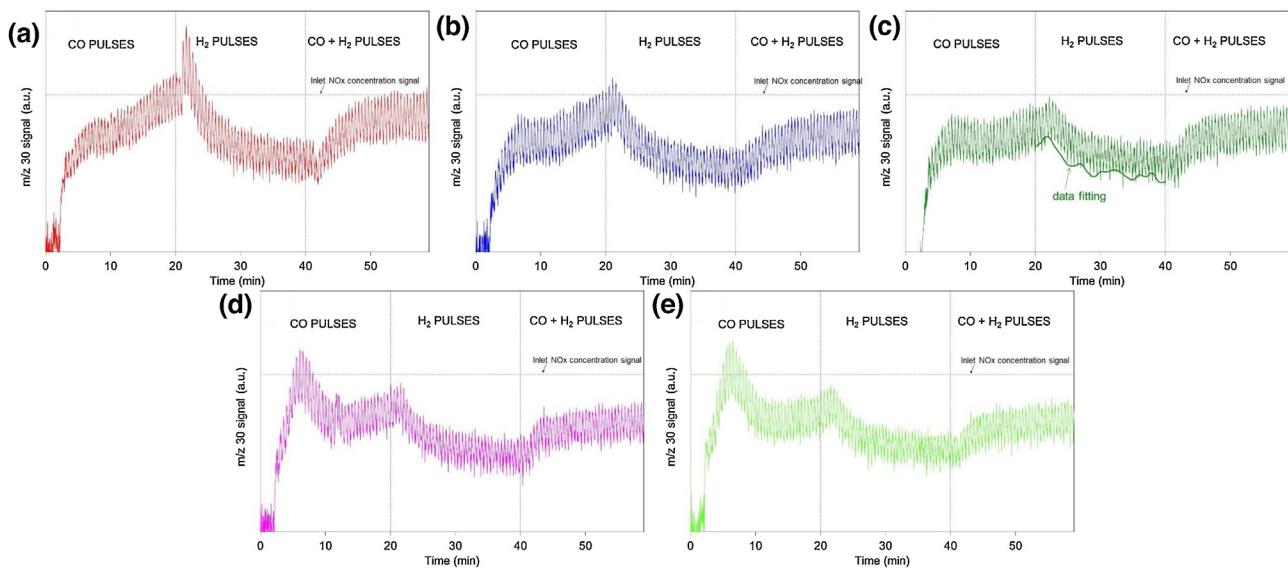


Fig. 5. m/z 30 signal (NOx) monitored during NSR experiments performed with (a) $\text{CuO}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$, (b) CuO/CeO_2 , (c) $\text{CuO}/\text{Ce}_{0.8}\text{Nd}_{0.2}\text{O}_8$, (d) $\text{CuO}/\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_8$, (e) $\text{CuO}/\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_8$.

were observed between different samples. Considering the NOx levels at the end of the series (after 15 min), the poorest results were obtained with $\text{CuO}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$ followed by CuO/CeO_2 , and the three catalysts with lanthanide dopants (La, Pr and Nd) behaved quite similarly and suffered less significant decreases in their NOx removal capacity with time. The interpretation of these differences are discussed in detail below, analysing the rapid-scan DRIFT spectra. However, a clear trend was that ceria doping with an acidic cation such as Zr^{4+} had a much worse effect on the extent of regeneration in CO than doping with basic cations such as La^{3+} , Pr^{3+} or Nd^{3+} .

The opposite trend was obtained during H_2 regeneration pulses (Fig. 6b). H_2 was able to regenerate all catalysts until stable NOx removal levels were achieved, and the most effective catalyst under these experimental conditions was $\text{CuO}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$, followed by CuO/CeO_2 and finally the three catalysts with lanthanide dopants (La, Pr and Nd).

Finally, using the $\text{CO} + \text{H}_2$ mixture (Fig. 6c) was less effective than pure H_2 alone but much better than pure CO. During the first 10 min of NOx removal under $\text{CO} + \text{H}_2$ pulses, the NOx fitting lines increased slightly, but after this time, stable levels were achieved with all catalysts. Differences among catalysts were minor, but it was still possible to distinguish that the catalyst with the most acidic dopant ($\text{CuO}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$) reached the lowest NOx removal level while the catalyst with the most basic dopant ($\text{CuO}/\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_8$) the highest levels.

Rapid-scan DRIFTS is a powerful tool to study the surface of the catalysts during the transient conditions of the NSR experiments. Figs. 7–9 show plots of the absorbance at selected wavenumbers monitored during pulses of CO, H_2 and $\text{CO} + \text{H}_2$ respectively. The profile of the m/z 30 signal has been included in these figures.

3.3.1. Rapid-scan DIRIFTS analysis during NSR experiments with CO pulses

All catalysts showed nitrate bands during the NSR experiments with CO pulses, and the signal of the maxima absorbance of the band due to nitrates at $\text{ca. } 1556\text{--}1500\text{ cm}^{-1}$ is plotted in Fig. 7. The other two nitrate bands that are expected to appear around 1250 and 1000 cm^{-1} were also observed, but are excluded for simplicity. The general profile shape of the m/z 30 signal and the nitrates band at $1556\text{--}1500\text{ cm}^{-1}$ were quite similar for all catalysts. Once a CO

pulse was fed (as indicated by vertical dashed lines) the m/z 30 signal showed a peak due to the NOx slip that occurred together with the reduction. This partially cleaned the catalyst, and the nitrates band intensity dropped to a minimum.

The rapid-scan spectra of the CuO/CeO_2 catalyst only showed bands due to nitrates (Fig. 7b), and the position at 1500 cm^{-1} was consistent with the formation of monodentate nitrates. This suggested that the NSR mechanism occurring over CuO/CeO_2 during CO pulses consisted of the chemisorption and subsequent reduction of nitrates (probably monodentate).

On the other hand, the catalysts with ceria dopants showed more complex behavior, which is not surprising because loading of foreign cations is expected to introduce heterogeneity into the chemisorption sites. The band at 1550 cm^{-1} could be attributed to bidentate nitrates, and the bands around $1485\text{--}1470\text{ cm}^{-1}$ could be assigned to monodentate nitrates. That is, the CuO/CeO_2 catalyst chemisorbed NOx leading to only one type of nitrate, while the doped catalysts were able to store nitrates of different configurations. The $\text{CuO}/\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_8$ catalyst (Fig. 7e) was the only one showing a band at 1360 cm^{-1} , and this feature, together with that at 1463 cm^{-1} could be assigned to carbonates.

The key point to explain the poor NSR behavior of the $\text{CuO}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$ catalyst (Fig. 6a) with CO pulses could be the formation of a species as detected by a band at 1438 cm^{-1} , which was only observed for this catalyst (Fig. 7a). This band may be assigned to monodentate nitrites, the formation of which would suggest that the oxidation capacity of $\text{CuO}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_8$ under CO-NSR conditions was poorer than the remaining catalyst, leading to the least effective NOx removal after some time in reaction.

3.3.2. Rapid-scan DIRIFTS analysis during NSR experiments with H_2 pulses

The absorbance of relevant bands monitored by rapid-scan DRIFTS during the NSR experiments with H_2 pulses are plotted in Fig. 8 together with the m/z 30 (NOx) and 28 (N_2) signals. The pulses of H_2 clean the catalysts surface and lead to NOx and N_2 release. These m/z 30 and 28 profiles confirm that a major proportion of the NOx stored on the catalysts is reduced to N_2 and that few NOx slips. It is worth noting that evidences of other reduction byproducts, like N_2O (m/z 44) or NH_3 (m/z 17) were not observed upon H_2 pulses. Unfortunately, this high selectivity towards N_2 formation as a NOx

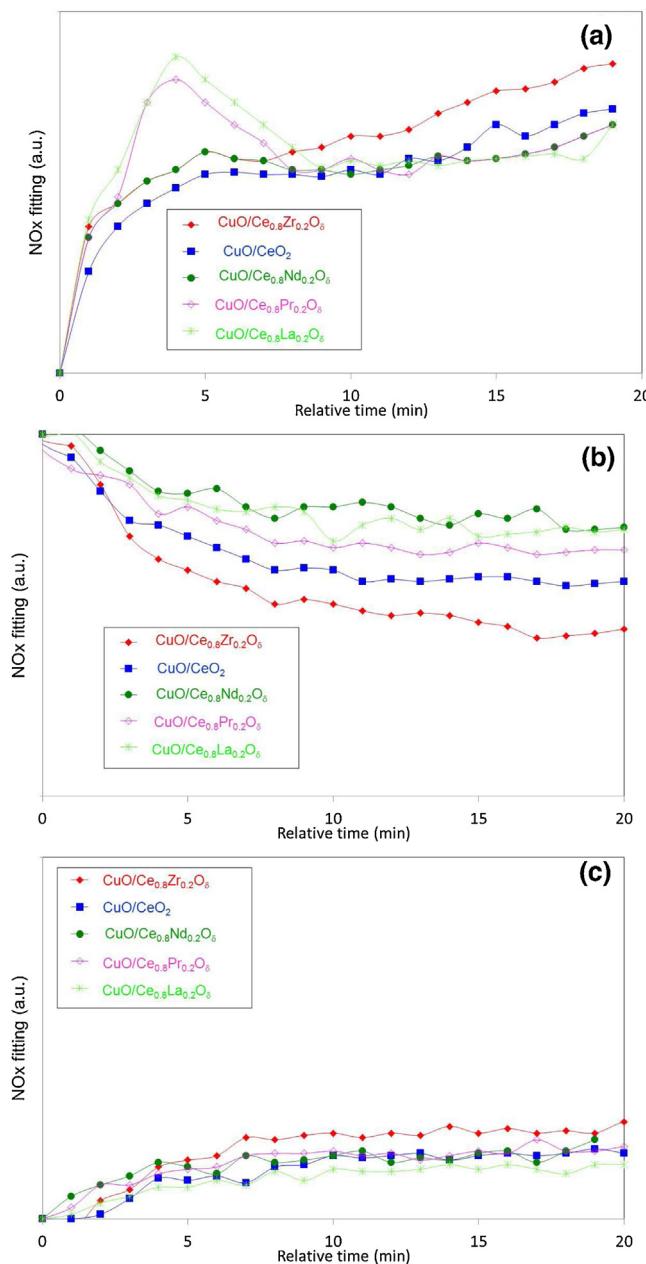


Fig. 6. NOx data of Fig. 5 fitting. NOx concentration at the beginning of each pulse was taken for the fitting, and concentrations were normalized by dividing all data of each series by the NOx concentration of the first point of the series. The time scales were set considering time = 0 at the beginning of the first pulse of each series. (a) CO pulses, (b) H₂ pulses and (c) CO + H₂ pulses.

reduction product observed for H₂ pulses was not confirmed for CO pulses, because both CO and N₂ contribute to the *m/z* 28 signal impeding monitoring of N₂.

All catalysts showed nitrate bands, and their absorbance at 1550–1500 cm^{−1} is plotted. In accordance with observations in CO-NSR experiments, the position of the nitrate bands for the CuO/CeO₂ catalyst during H₂ pulses (Fig. 8b, 1500 cm^{−1}) is consistent with the presence of monodentate nitrates, while the frequency of bands for the doped catalysts (around 1550 cm^{−1}) would suggest the formation of bidentate nitrates.

The catalysts with lanthanide dopants (La, Pr and Nd; Fig. 8e, d and c respectively) only showed bands due to bidentate nitrates, while the CuO/Ce_{0.8}Zr_{0.2}O₆ (Fig. 8a) and CuO/CeO₂ (Fig. 8b) catalysts presented more complex spectra. CuO/Ce_{0.8}Zr_{0.2}O₆ (Fig. 8a)

additionally involved nitrites (band at 1438 cm^{−1}) and monodentate nitrates (band at 1485 cm^{−1}), but in this case, the low oxidation capacity of CuO/Ce_{0.8}Zr_{0.2}O₆ as deduced from the presence of such nitrites seems largely irrelevant for NOx removal, because CuO/Ce_{0.8}Zr_{0.2}O₆ was the most effective catalyst removing NOx in H₂ pulse experiments (Fig. 6b). The more effective regeneration achieved with H₂ with respect to CO would mask other effects.

The absorbance of the hydroxyls band at 3615–3605 cm^{−1} only changes for the CuO/Ce_{0.8}Zr_{0.2}O₆ (Fig. 8a) and CuO/CeO₂ (Fig. 8b) catalysts. Hydroxyls could be formed by H₂O (H₂ oxidation product) chemisorption on reduced sites of ceria. It is known that hydroxyls are suitable chemisorption sites for NOx, but it seems that this is not occurring in these experiments (Fig. 8a and b). If NOx were chemisorbed on hydroxyls, the hydroxyls and nitrite/nitrate bands should follow opposite trends, and this is not the case. The nitrites, nitrates and hydroxyls bands follow the same patterns, and this means that all these species are formed and depleted simultaneously. One hypothesis to explain this would be that NOx and H₂O compete for the chemisorption sites of the catalysts once they are available after the H₂ pulse. H₂O is more basic than NOx, and this would explain why H₂O is not chemisorbed on catalysts with basic dopants (Pr, Nd or La; Fig. 8e, d and c respectively) but only on CuO/Ce_{0.8}Zr_{0.2}O₆ (Fig. 8a), and CuO/CeO₂ (Fig. 8b). Also, the peaks shapes of the absorbance band due to nitrates (Fig. 8a and b) are much narrower and sharper than those obtained for catalysts with basic dopants (La, Pr and Nd; Figs. 8e, d and c respectively), and this indicates that regeneration of CuO/Ce_{0.8}Zr_{0.2}O₆ and CuO/CeO₂ by H₂ is much more effective than regeneration of La, Pr or Nd containing catalysts. This better regeneration would explain the best performance by CuO/Ce_{0.8}Zr_{0.2}O₆, followed by CuO/CeO₂, observed in Fig. 6b and also that H₂O is more likely to become chemisorbed on these two catalysts.

In conclusion, H₂ is more effective than CO in regenerating all catalysts, and sample containing the acidic dopant (CuO/Ce_{0.8}Zr_{0.2}O₆) is regenerated by H₂ better than those with more basic dopants (La, Pr and Nd).

3.3.3. Rapid-scan DRIFTS analysis during NSR experiments with CO + H₂ pulses

Rapid scan DRIFTS monitoring indicated that the catalysts during NSR experiments with CO + H₂ pulses (Fig. 9) show some features of H₂-NSR and others of CO-NSR.

The CuO/Ce_{0.8}Zr_{0.2}O₆ catalyst showed DRIFTS bands (Fig. 9a) consistent with the participation of monodentate (1485 cm^{−1}) and bidentate (1556 cm^{−1}) nitrates, monodentate nitrites (1435 cm^{−1}) and hydroxyls (3615 cm^{−1}). As deduced from experiments performed with individual reductants, the participation of nitrites could be related to the poorer oxidation activity of this catalyst, and this had a negative effect on the CO-NSR but not on the H₂-NSR. The lower oxidation capacity of CuO/Ce_{0.8}Zr_{0.2}O₆ also affected the behavior while using pulses of CO + H₂ (Fig. 6c), and would explain the lowest extent of NOx removal achieved with this catalyst.

The changes in the absorbance bands due to hydroxyls on CuO/Ce_{0.8}Zr_{0.2}O₆ and CuO/CeO₂ during CO + H₂ pulses (Fig. 9a and b respectively) are less significant than those observed with pure H₂ pulses (Fig. 8a and b) due to the lesser amount of H₂ involved. On the other hand, and in accordance with the experiment performed with pure CO, in experiments with CO + H₂ pulses, the CuO/Ce_{0.8}La_{0.2}O₆ catalyst was the only one showing a band at 1360 cm^{−1} due to carbonates.

In conclusion, the regeneration of the catalysts with the CO + H₂ mixture (Fig. 6c) presented intermediate behavior between CO-NSR (Fig. 6a) and H₂-NSR (Fig. 6b), with similarities to the NOx removal trends observed with pure CO pulses but with smaller differences

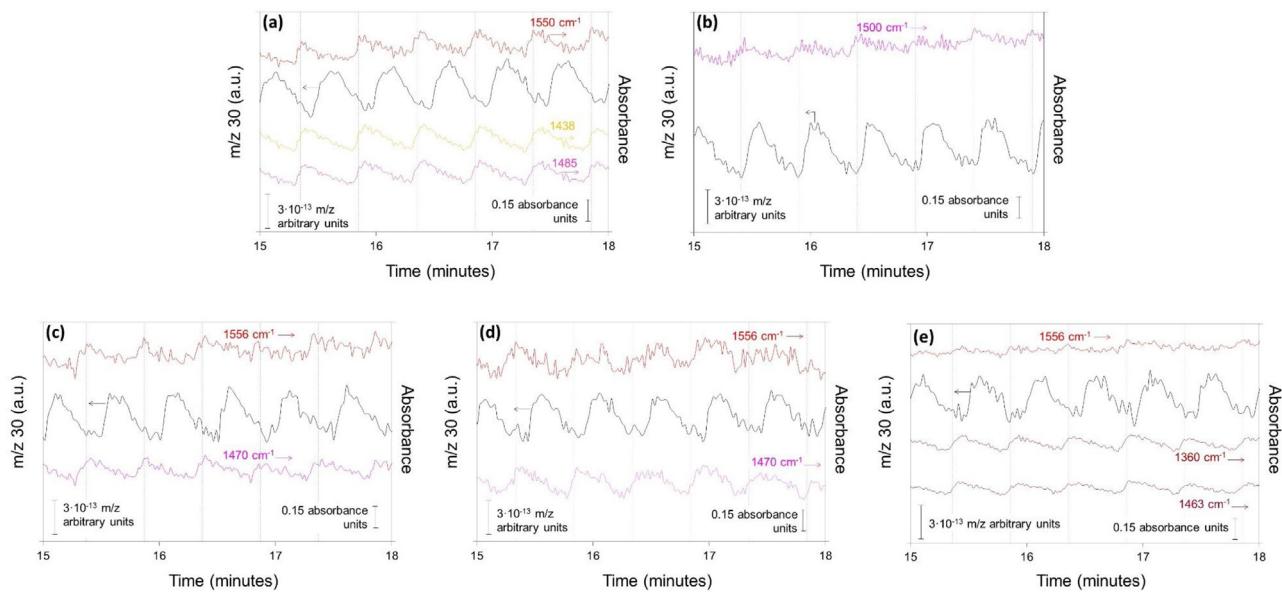


Fig. 7. m/z 30 (NO_x) and absorbance at selected wavenumbers monitored during NSR experiments with CO pulses by fast DRIFTS screening for (a) CuO/Ce_{0.8}Zr_{0.2}O_δ, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O_δ, (d) CuO/Ce_{0.8}Pr_{0.2}O_δ, (e) CuO/Ce_{0.8}La_{0.2}O_δ. Vertical dashed lines indicate when a CO pulse was introduced.

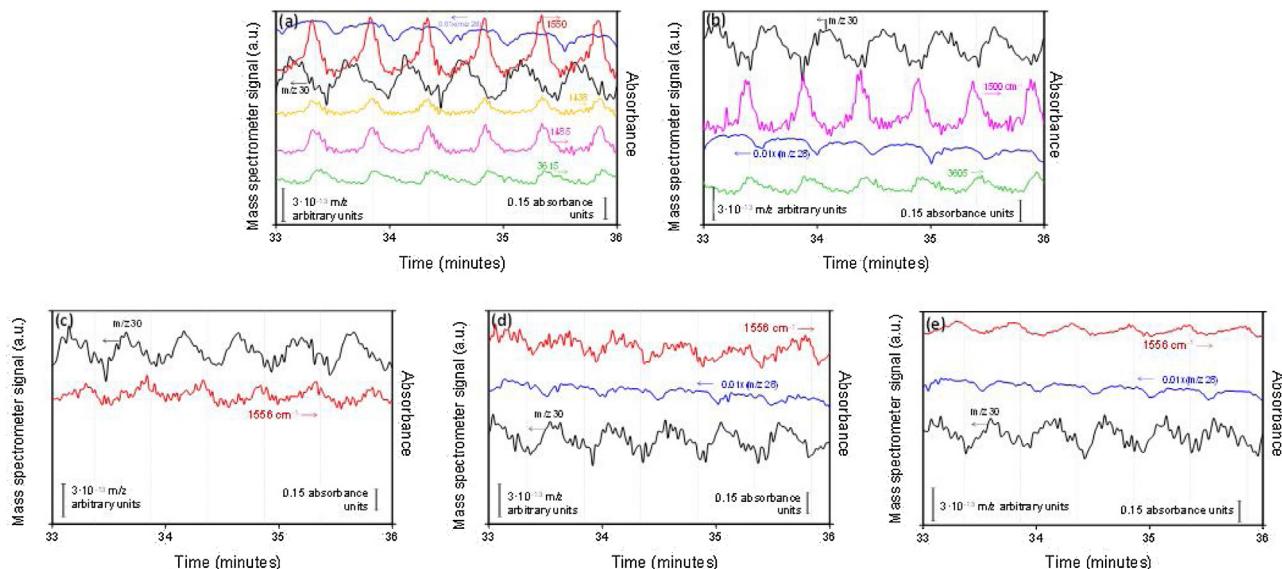


Fig. 8. m/z 30 (NO_x), 28 (N₂) and absorbance at selected wavenumbers monitored during NSR experiments with H₂ pulses by fast DRIFTS screening for (a) CuO/Ce_{0.8}Zr_{0.2}O_δ, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O_δ, (d) CuO/Ce_{0.8}Pr_{0.2}O_δ, (e) CuO/Ce_{0.8}La_{0.2}O_δ. Vertical dashed lines indicate when a H₂ pulse was introduced. The baseline of the m/z 28 signal has been subtracted before plotting.

amongst catalysts. The rapid-scan DRIFTS monitoring confirms this intermediate behavior in the CO + H₂ mixture.

4. Conclusions

Copper catalysts with Ce_{0.8}M_{0.2}O_δ supports (M = Zr, La, Ce, Pr or Nd) were studied by *operando* rapid-scan DRIFTS for NSR with high frequency (30 s) CO, H₂ and CO + H₂ micropulses, and the following conclusions can be drawn:

- In the absence of reductant pulses, NO_x was stored on the catalysts as nitrite and nitro groups below 200–250 °C, and above this temperature nitrites were not identified and nitrates were the predominant species. The thermal stability of the NO_x species

stored on the catalyst showed a dependence on the acid/basic character of M:

More acidic/less stable Zr⁴⁺ < none < Nd³⁺ < Pr³⁺ < La³⁺ More basic/more stable

- The regeneration of the catalysts in the NSR experiments was better with H₂ than with CO, and the CO + H₂ mixture presented an intermediate behavior with the NO_x removal trends observed with pure CO pulses but with smaller differences among catalysts. N₂ is the main NO_x reduction product upon H₂ regeneration.
- The best NO_x removal in NSR experiments performed at 400 °C with CO + H₂ pulses was achieved with the catalyst with the most basic dopant (CuO/Ce_{0.8}La_{0.2}O_δ) while the poorest NO_x removal

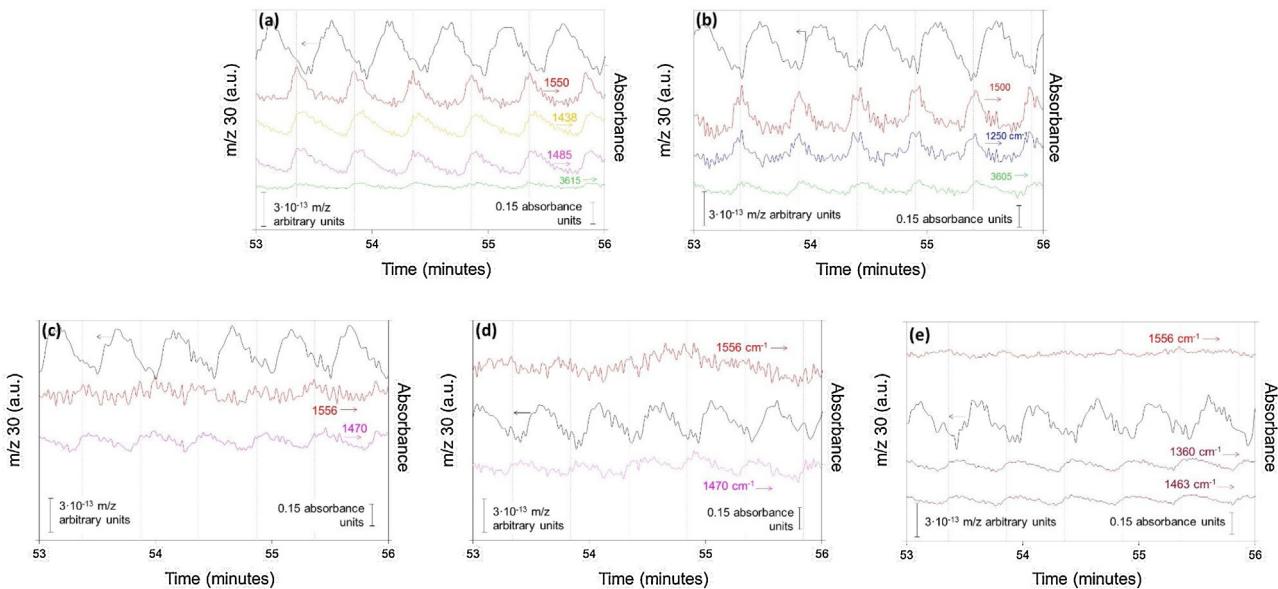


Fig. 9. m/z 30 (NO_x) and absorbance at selected wavenumbers monitored during NSR experiments with CO + H₂ pulses by fast DRIFTS screening for (a) CuO/Ce_{0.8}Zr_{0.2}O₈, (b) CuO/CeO₂, (c) CuO/Ce_{0.8}Nd_{0.2}O₈, (d) CuO/Ce_{0.8}Pr_{0.2}O₈, (e) CuO/Ce_{0.8}La_{0.2}O₈. Vertical dashed lines indicate when a CO + H₂ pulse was introduced.

level was achieved with the catalyst with the most acidic dopant (CuO/Ce_{0.8}Zr_{0.2}O₈).

- In comparison to catalysts with basic dopants (La, Pr and Nd), the poor behavior of the CuO/Ce_{0.8}Zr_{0.2}O₈ catalyst in NSR experiments with CO pulses was attributed to its lower NO oxidation capacity under these conditions. CuO/Ce_{0.8}Zr_{0.2}O₈ yielded both nitrites (N(III)) and nitrates (N(V)) upon NO_x chemisorption in NSR experiments with CO pulses while the other catalysts did not yield nitrites, but only nitrates (N(V)).

Acknowledgements

The authors thank the financial support of Generalitat Valenciana (Project PROMETEOII/2014/010 and grant BEST/2014/250), the Spanish Ministry of Economy and Competitiveness (Projects CTQ2015-67597-C2-2-R, MAT2014-61992-EXP, and grant PRX14/00249), and the UE (FEDER funding). We thank Dr. A.J. McCue (University of Aberdeen) for support involving the experimental set-up.

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